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Methanol steam reforming for hydrogen generation via conventional and membrane reactors: A review

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ABSTRACT

In the recent years, hydrogen has gained a considerable interest as an energy carrier useful for various applications and, particularly, for polymer electrolyte membrane fuel cells (PEMFCs) supply. Nevertheless, PEMFCs require high purity hydrogen as a feeding fuel, which shows some limitations regarding storage and transportation. Therefore, to overcome these problems, the in situ hydrogen generation has made attractive both alcohols and hydrocarbons steam reforming reaction. Among other fuels, methanol is an interesting hydrogen source because it is liquid at ambient conditions, possesses relatively high H/C ratio, low reforming temperature (200–300 °C) and it is also producible from biomass. Meanwhile, there is a comprehensive literature about inorganic membrane reactors utilization for hydrogen generation via methanol steam reforming reaction. This review illustrates the earlier state of the art from an experimental point of view about hydrogen production from methanol reforming performed in both conventional and membrane reactors. Furthermore, a short overview about methanol reforming catalysts as well as a discussion on the impact of methanol steam reforming process via inorganic membrane reactors to produce hydrogen for PEMFCs supply is given.

Contents

1. Introduction

During the last decades, there has been a growing interest on developing technologies taking advantage of clean energy sources. The reduction of atmospheric pollution and, namely, the emission of greenhouse gases have become imperative and, among the new

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technologies for mitigating these emissions, fuel cells have the ability to efficiently convert chemical into electrical energy. In particular, PEMFCs are zero-pollutants emission systems because they transform the chemical energy of the electrochemical reaction within hydrogen and oxygen into clean electrical power [1,2]. Generally, they work at $T<100\,^{\circ}C$, making possible a rapid start-up. Unfortunately, as a principal drawback, PEMFCs need to be supplied by high purity hydrogen since the anodic Pt-based catalyst tolerates less than 10 ppm of CO. The hydrogen is industrially produced as a hydrogen-rich stream mainly via steam reforming of natural gas in conventional reformers (CRs) [3]. Successively, hydrogen is purified to reach the desired purity for the PEMFC supply. Indeed, the reformed stream coming out from the CRs commonly contains hydrogen, CO_2, CO, CH_4 and other byproducts. As a consequence, PEMFCs supply imposes the purification of hydrogen, which commonly takes place in second stage processes, namely water gas shift (WGS) reaction (performed in two reactors operating in series at high and low temperatures), partial oxidation (PROX) and pressure swing adsorption (PSA) [4–6]. Nevertheless, the aforementioned stages of hydrogen purification affect negatively the overall process in terms of costs and efficiency [7]. Hence, at scientific level much attention has gained the development of alternative technologies to generate high purity hydrogen (or, at least, CO_x-free) for PEMFCs supply. Among them, membrane reactors (MRs) technology plays an important role as an alternative solution to the conventional systems (CRs+further stage of hydrogen purification systems) in terms of combination in a single stage of the reforming reaction for generating hydrogen and its purification without needing any further process/treatment [8]. As shown in Fig. 1, the interest towards this technology is testified by the growing number of scientific publications in the specialized literature.

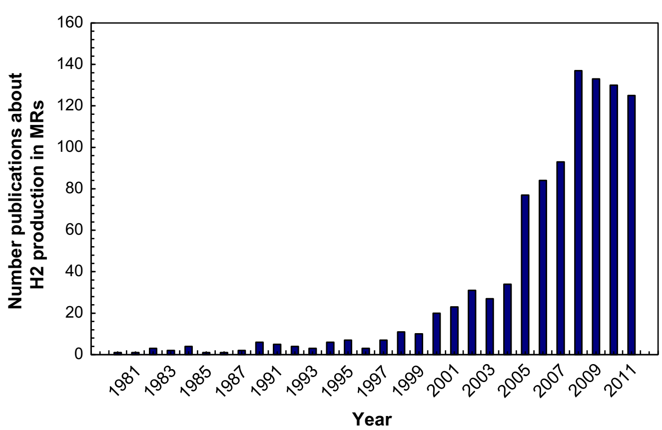


Fig. 1. Number of scientific papers on H_2 production by MR technology vs year. Scopus database: www.scopus.com.

As a particular aspect regarding membrane technology, the inorganic MRs utilization makes possible several benefits over the CRs [10–12], although they also present some drawbacks as summarized in Table 1.

In particular, in the last decades, an extensive literature has been addressed to hydrogen production using inorganic MRs based on both dense and supported Pd-based membranes [13–25], because of their high perm-selectivity to hydrogen with respect to all other gases.

Meanwhile, compared to other feedstocks, methanol exploitation shows various advantages as a hydrogen carrier for fuel cell applications and, namely, it can be produced from renewable sources [9] and the reforming reaction occurs at relatively low temperatures, ca. 240–260 °C [4], compared to the methane reforming, normally performed at 800–1000 °C [10]. Methanol steam reforming (MSR) reaction has been seen as a very attractive and promising process for hydrogen production and, according to the scientific literature on the argument, it can be described by the following chemical reactions:

$$CH_3OH+H_2O=CO_2+3H_2 \quad \Delta H^{\circ}_{298\,K}=+49.7\ (kJ/mol) \tag{1}$$

$$CO+H_2O=CO_2+H_2 \quad \Delta H^{\circ}_{298\,K}=-41.2\ (kJ/mol) \tag{2}$$

$$CH_3OH=CO+2H_2 \quad \Delta H^{\circ}_{298\,K}+90.7\ (kJ/mol) \tag{3}$$

Reaction (1), represents MSR reaction, reaction (2) represents water gas shift reaction and reaction (3) represents the methanol decomposition reaction. Only the WGS reaction is exothermic and takes place without variation of moles number. The steam reforming reaction besides being endothermic takes place with an increase of moles number. Unfortunately, the main drawback of this process is represented by the CO formation as a byproduct, which – as stated previously – can poison the anodic catalyst of the PEMFCs as well as affect negatively the permeation of Pd-based MRs [26]. Indeed, in the field of MSR reaction performed in CRs, several scientists paid special attention to catalyst optimisation in order to reduce the CO content [27–38].

The aim of this review is then oriented in describing the earlier state-of-the-art about the use of inorganic MRs technology for conducting the MSR reaction targeting the production of PEMFC grade hydrogen.

2. Methanol steam reforming catalyst

MSR has been widely studied and the most common catalysts are based on copper, such as $Cu/ZnO/Al_2O_3$, working at ca. 240–260 °C [27,39,40]. Copper-based catalysts are very active and low cost, even though they originate a significant concentration of carbon monoxide, show low stability and pyrophoric nature. As an example, Conant et al. [41] studied $CuO/ZnO/Al_2O_3$ catalyst stability at 250 °C and concluded that, after 60 h of operation, methanol

Table 1
Some of the most significative benefits and drawbacks of MRs utilization.

MRs benefits	MRs drawbacks
Compact unit in combining both reaction and hydrogen purification with a consequent capital costs reduction	High costs and low mechanical resistance in case of dense palladium-MRs
Conversion enhancement of equilibrium limited reactions. Higher conversions than CRs (exercised at the same MRs conditions) or at the same conversion of CRs reached at milder operating conditions	Not high purity hydrogen production in the case of composite Pd-based MRs. Not high hydrogen perm-selectivity in the case of non Pd-based MRs utilization
Direct production of high purity hydrogen in a single unit (in the case of a dense Pd-based MR)	Hydrogen embrittlement at $T<300\,^{\circ}C$ in the case of dense Pd-MRs
Retentate stream of MRs rich in CO_2 (i.e. the stream not permeated through the membrane) when performing reforming reactions	Contamination of H_2S, coke CO, etc. in the case of Pd-MRs

conversion dropped 40%. Catalyst deactivation can be then caused by sintering, coke deposition, catalyst poisoning (chloride, sulphur) and change in oxidation state. Coke formation can be prevented using the water molar fraction above the stoichiometry (Eq. (1)) and, generally, the best results are obtained for molar water/methanol ratio of 1.5:1.

Therefore, the development of MSR catalysts more active, stable and producing less carbon monoxide are needed. Especially, catalysts that can operate at ca. 180 °C are strongly desired since they are expected to be more stable and to produce less carbon monoxide (Eq. (3) is disfavored for lower temperatures) and thermodynamically they show almost complete conversion. Moreover, since MSR is an endothermic reaction, the reformer reactor can be synergistically coupled with a high temperature (HT)-PEMFC, which works exothermally. HT-PEMFC operates preferentially in the range 160 °C and 180 °C. Despite the advantages of working at 180 °C, copper based catalysts need activation that occurs naturally when operating the reactor at temperatures above 240 °C. For $CuO/ZnO/Al_2O_3$, this is carried out by reducing the catalyst under hydrogen atmosphere at 250 °C.

Two approaches can be followed to prepare copper-based more active catalysts and originating less carbon monoxide: (a) adding promoters [42–45] and (b) changing the preparation method [46,47]. Both approaches are used to increase the metal dispersion and surface area and to decrease the particle size. The most used promoters for copper-based catalysts are ZnO [42], ZrO_2 [48], Mn [49], CeO_2 [50] or Al_2O_3 [51]. Furthermore, some materials can affect the CO selectivity such as ZrO_2 [42] or change the surface area where copper is dispersed such as alumina or chromium(III) oxide [52]. The catalyst preparation method is the second tool available for improving the catalytic activity and the most used for cooper-based catalysts are derivations from co-precipitation and wet-impregnation. Depending on the promoters or the supports, the more active catalyst of a specific type can be obtained by one or other method or even by a derivation of the previous (e.g. to produce $CuZrO_2$ the best method is a derivation from co-precipitation [53–55]). Alumina is one of the most used catalyst support, but there are others such as carbon nanotubes that are being investigated with promising results [56]. Furthermore, other interesting results were presented by Gao et al. [57] using a La_2CuO_4 nanofiber.

Besides cooper-based catalysts, others are being studied for MSR reaction, in particular those containing group VIII–X metals and, especially, palladium. $Pd/ZnO/Al_2O_3$ catalyst presents higher stability than $Cu/ZnO/Al_2O_3$ with an initial deactivation of 17%, afterwards stable for 60 h [41]. Pd/ZnO catalyst when compared with other metals (Ni, Pt, Ru, Ir) supported on ZnO, presents lower CO production and a higher methanol conversion [58–61]. The application of a second metal to form bimetallic alloy can also improve the catalyst activity and selectivity. The best activity reported was obtained with Pd/Zn and Pd/Ga and the best selectivity with Pd/Cd [56]. Pd catalysts are drawing the attention of many researchers that are investigating the role of the preparation methods [62], the effect of support surface area [63] and the particle size [64]. The search for more active and selective catalysts for MSR resulted in a large number of articles that were recently reviewed [65].

3. Methanol steam reforming reactors

The reactor design has direct impact on the reaction conversion, but owing to higher technical complexity and manufacturing costs of other designs, the reformers and MRs are normally tubular. However, recent efforts in the area of micro-processing made possible and easier to manufacture other reactor designs and namely well-structured flat micro-reactors. A micro-reactor is defined as a device that contains micro structured features, with a sub-millimeter dimension, in which chemical reactions are performed in a continuous manner [66]. They present advantages compared to conventional ones such as higher surface-to-volume ratio, smaller mean distance of the specific fluid volume to the reactor walls, better heat and matter transfer properties and flow patterns that fit with the reaction needs. Furthermore, flat reformers are suitable for stack integration with fuel cells.

Packed-bed micro-reactors require well-define catalyst particles, with regular shape and much smaller than the internal dimensions of the micro-channels, which is a problem for most of commercial catalysts [66] and, then, most of micro-reactors use the catalyst applied as a coat. Micro-reactors range in area from 0.1 to 10 cm^2 [66] and mini-reactors range between 10 and 200 cm^2. Mini-reactors, however, are more suitable for packed bed applications and match the typical size of fuel cells.

MSR originates a stream that contains besides hydrogen, small amounts of reactants, carbon dioxide and carbon monoxide. The reformate stream needs, then, to be purified and dense Pd-membrane reactors not only allow obtaining a high purity hydrogen stream but also contribute for improving the reformer conversion. Pd-membrane reactors are normally tubular, even though they can also be produced flat [22,67].

Many studies have been developed to explore the advantages of micro/mini-reactors to produce hydrogen through MSR. The design of a reactor targets the maximization of the conversion and selectivity at the lowest costs and its performance is influenced by the flow pattern, velocity profile, pressure drop and heat transfer, so all these aspects must be considered [68]. For conducting MSR reaction, most of the used reactor designs are rectilinear channels, pin-hole, coil-based and radial (Fig. 2).

Coil-based reactor designs allow high conversions, but impose a significant pressure drop penalty, which may be a limitation for compact applications [68]. In the other hand, the rectilinear channel designs exhibit a small-pressure drop, but the conversion is low due to uneven mass distribution and is affected by the Reynolds number [68]. Yet, by adjusting the channels width [69] or by imposing a pressure drop at the channels entrance even distributions on rectilinear channel designs can be obtained, improving the methanol conversion [69]. The pinhole design has

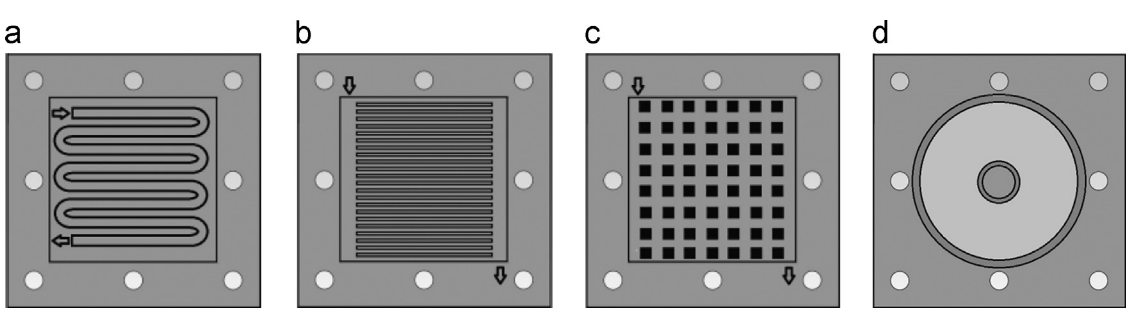


Fig. 2. Different flow field designs of CRs. (a) coiled-serpentine; (b) Parallel multichannel; (c) Pin-hole; (d) Radial.

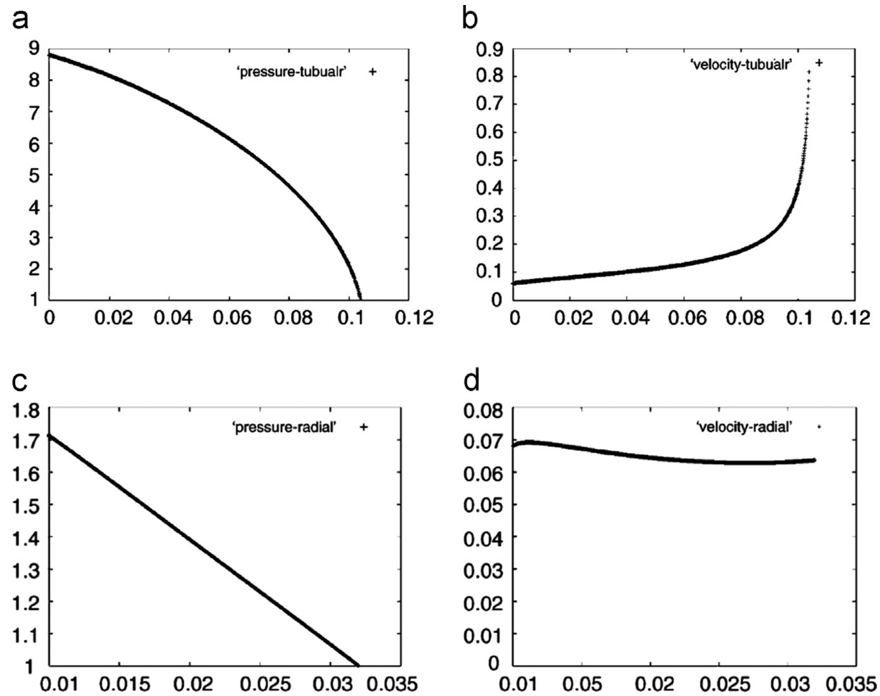


Fig. 3. (a) Pressure profile in micro-channel reactor—fluid pressure (atm) vs. distance (m); (b) velocity profile in micro-channel reactor—fluid velocity (m/s) vs. distance (m); (c) Pressure profile in radial reactor—fluid pressure (atm) vs. distance (m); (d) velocity profile in radial reactor—fluid velocity (m/s) vs. distance (m), (adapted from [70]).

great potential for innovative applications; it presents a methanol conversion comparable to the coil reactor with lower pressure drop. This design, however, exhibits a mass distribution that depends on the Reynolds number. The flow field design should provide even a distribution, independently of the Reynolds number, since the reactor is operated at different flow rates.

Typically, the molar flow rate of reformate streams is almost twice the feed flow rate, originating a significant surface velocity increase as the reaction stream moves along a constant cross sectional area reactor. Moreover, since the pressure decreases towards the exit of the reactor, the surface velocity increases even more [70] (Fig. 3). For a diffusion-limited or close to diffusion-limited reaction, this large variation of surface velocity can be very detrimental for the conversion [71].

The radial reactor design, Fig. 2d, has unique features for MSR because of the increase of section area as the gas moves to the outlet, leading to low pressure drop compared to tubular reactor and a close to constant velocity profile (Fig. 3). Radial reactor designs despite of the complex manufacturing originate higher methanol conversions than channel designs [70].

The reactor design must minimize temperature gradients, operating as close as possible of isothermal conditions. For channel reactors, assuming only inter-particle temperature gradients, isothermal conditions can be achieved by diminishing the channel width [72,73]. However, the width of the channels should be ca. 300 μm in the case of MSR to avoid temperature gradients [72], which is not feasible for packed bed reactors, due to high-pressure drop originated by the small particle size of the catalyst.

To minimize temperature gradients some strategies have been considered such as internal heating [74] or wall coated reformers [75–80]. Wall-coated reformers compared to packed-bed show low-pressure drop and high heat transfer providing isothermal conditions, but they have lower specific catalyst load. Nevertheless, regarding the conversion and for a given contact time (*W*/*F*), some studies indicate that wall-coated reformers better perform [72,78,79], while others indicate similar performances [80]. These different conclusions might be related to differences in catalyst-layer packing or coating methods, catalyst weight, channel width and operating conditions [81]. Inside the catalyst layer, heat transfer is dominated by heat conduction (e.g. $\lambda_{CuO/ZnO/Al_2O_3} = 0.17\ W\ m^{-1}\ K^{-1}$ [72]), thus using glass beads or other inert particles with higher heat conductivity should improve the temperature distribution.

4. Outlook on membrane reactor technology and fuel cells

4.1. Membrane reactors

The comprehensive concept of MRs was introduced in the 1950s, even if only with the exploitation of new inorganic materials and the development of high-temperature membrane processes there has been a growing interest towards the research and application of MR technology [82]. In fact, this is testified by an extensive literature on MRs concerning different applications and scientific fields. In detail, during the last 30 years different kind of MRs have been developed and, as a general subdivision, they are summarized in the following:

(a) Dense and porous inorganic membrane reactors [83,84].
(b) Zeolite membrane reactors [85,86].
(c) Polymeric membrane reactors [87,88].
(d) Enzyme membrane reactors [89]
(e) Bio-medical membrane reactors or membrane bio-reactors using cells [90,91].
(f) Electrochemical membrane reactors (fuel cells, electrolytic cells, etc.) [92].
(g) Photo-catalytic membrane reactors [93].

Recently, many scientists have proposed the application of membranes combined to chemical and biochemical reactions in order to intensify the whole process. Most of the approaches may be classified concerning the role of membranes towards the removal/addition of the various chemical species as: (a) extractor, (b) distributor and (c) contactor. Membranes are generally categorized by referring to materials or structures, giving particular relevance to the selectivity of the permeation of such a product

with respect to other ones. However, in this review our attention is devoted to the discussion on dense and porous inorganic membrane reactors, able to integrate a chemical reaction (such as MSR) with a membrane process (H_2 separation). Commonly, the role of the membrane in a membrane reactor can be described as:

- Extractor, when it selectively removes the desired products from the reaction mixture for permeation.
- Distributor, when it controls the addition of reactants to the reaction mixture.
- Contactor, when it intensifies the contact within reactants and catalyst.

When a MR is performed in "extractor" mode, a desired product obtained by the chemical reaction is selectively removed from the reaction side for permeation through the membrane. In the case of thermodynamic limited reactions, Extractor mode can also be used to increase the selectivity towards a particular intermediate species in a cascade reaction, if this species is selectively removed from the reaction medium. Furthermore, besides the benefit of the shift effect, the extractor modality may reduce sequential reactions. In particular, when the reaction rate of the undesired secondary reactions is higher than that of the main reaction, the reaction selectivity can be significantly increased by removing the desired intermediate species. Extractors have great application on dehydrogenations or reactions for hydrogen production such as steam reforming or WGS, performed using hydrogen selective membranes [94].

"Distributor" mode concerns the membrane utilization to add uniformly a limiting reactant along the reactor space to prevent hot spots and side reactions. For example, in partial oxidation reactions, the membrane is used for selectively dosing oxygen targeting both high conversions and product selectivities [95,96]. As a further benefit, considering that the reactants and oxygen are not premixed, mixtures are consequently avoided and flame back firing into the feed is prevented.

MRs used in "contactor" mode make possible that the two-sided geometry of the membranes may allow for different options to bring reactants into contact.

4.2. Palladium-based MRs

Among the inorganic membranes, special attention should be paid to dense palladium-based membranes owing to their full hydrogen perm-selectivity. Nevertheless, between 0 and 700 °C other metals such as niobium, vanadium and tantalum show higher hydrogen permeability than palladium, even if they have a stronger surface resistance to hydrogen transport than palladium. Therefore, dense palladium membranes are greatly considered, although their commercialization is limited by some drawbacks such as low hydrogen permeability and high costs [22]. The hydrogen molecular transport in palladium membranes takes place through a solution/diffusion mechanism, developed in six different activated steps: (a) dissociation of molecular hydrogen at the gas/metal interface; (b) adsorption of the atomic hydrogen on membrane surface; (c) dissolution of atomic hydrogen into the palladium matrix; (d) diffusion of atomic hydrogen through the membrane; (e) re-combination of atomic hydrogen to form hydrogen molecules at the gas/metal interface; (f) desorption of hydrogen molecules. Generally, the hydrogen flux permeating through a generic membrane may be expressed as in the following:

$$J_{H_2} = Pe_{H_2}(p^n_{H_2,\text{retentate}} - p^n_{H_2,\text{permeate}})/\delta \quad (4)$$

where J_{H_2} is the hydrogen flux permeating through the membrane, Pe_{H_2} the hydrogen permeability, δ the membrane thickness, $p_{H_2-\text{retentate}}$ and $p_{H_2-\text{permeate}}$ the hydrogen partial pressures in the retentate (reaction side) and permeate (side in which hydrogen permeating through the membrane is collected) zones, respectively, n (variable in the range 0.5–1) the dependence factor of the hydrogen flux on the hydrogen partial pressure. For membranes with thickness higher than 5 μm, Eq. (4) becomes the Sieverts–Fick law (5):

$$J_{H_2,\text{Sieverts-Fick}} = Pe_{H_2} \times (p^{0.5}_{H_2,\text{retentate}} - p^{0.5}_{H_2,\text{permeate}})/\delta \quad (5)$$

For high pressures the hydrogen-hydrogen interactions in the palladium bulk are not negligible, thus n becomes equal to 1:

$$J_{H_2} = Pe_{H_2} \times (p_{H_2,\text{retentate}} - p_{H_2,\text{permeate}})/\delta \quad (6)$$

Furthermore, if the hydrogen permeability is expressed as an Arrhenius-like equation, Sieverts–Fick law becomes the Richardson's Eq. (7):

$$J_{H_2} = Pe^0_{H_2}[\exp(-E_a/RT)] \times (p^{0.5}_{H_2,\text{retentate}} - p^{0.5}_{H_2,\text{permeate}})/\delta \quad (7)$$

when dense Pd-based membranes are exposed to pure hydrogen permeation below both 300 °C and 2.0 MPa, the so called "hydrogen embrittlement" phenomenon may take place. It may be solved by alloying palladium with other metals, such as silver, which displays its electron donating behaviour, being largely similar to that of the hydrogen atom in palladium, making possible competition for the filling of electron holes within the silver and hydrogen. In MRs, the presence of hydrogen sulfide, SO_2, Hg vapour, thiophene, arsenic, unsaturated hydrocarbons, or chlorine carbon from organic materials, etc. may contaminate dense Pd-based membranes causing their irreversible poisoning [97]. Furthermore, the presence of CO in a MR affects negatively the hydrogen permeation performances of the membrane, because the adsorbed CO displaces the adsorbed hydrogen, blocking the hydrogen adsorption sites. This effect is more intense at lower temperature (below 150 °C) or at higher CO feed concentration [98,99]. Also steam may poison dense Pd-based membranes by affecting the water vapour dissociation/recombinative desorption, which contaminates the palladium surface with adsorbed oxygen [100].

During the last years, special attention has been devoted to composite Pd-based MRs in order to reduce the amount of palladium and consequently lowering the cost. Composite membranes are constituted by a thin dense layer of palladium or its alloy deposited onto porous supports such as porous Vycor glass (silica gel), SiO_2, Al_2O_3, and B_2O_3 or porous stainless steel (PSS). The supports having a thermal expansion coefficient close to the palladium allow high mechanical durability and simplify the gas sealing [16]. Nevertheless, PSS support alloys the palladium at relatively high temperatures, leading to lower the hydrogen permeability [101].

4.3. Proton exchange membrane fuel cells

PEMFCs gained a considerable attention because they represent an alternative technology to produce green power due to the chemical energy conversion of a fuel such as hydrogen directly into electrical energy [102]. Indeed, PEMFCs could represent a viable solution to these issues because they are able to limit CO_2 and other harmful emissions in the atmosphere. Unfortunately, PEMFCs show also some drawbacks to enter fully in the market such as the high cost of the membrane, fuel crossover, anodic catalyst poisoning mainly caused by the CO and so on. PEMFCs are commonly exercised at $T < 100$ °C and ambient pressure using commercial membranes based on Nafion (produced by DuPont) as a sulfonated perfluorinated polymer. Nafion shows great performances in terms of proton conductivity and high potential at low-medium temperature (up to 80–100 °C) and under fully hydrated

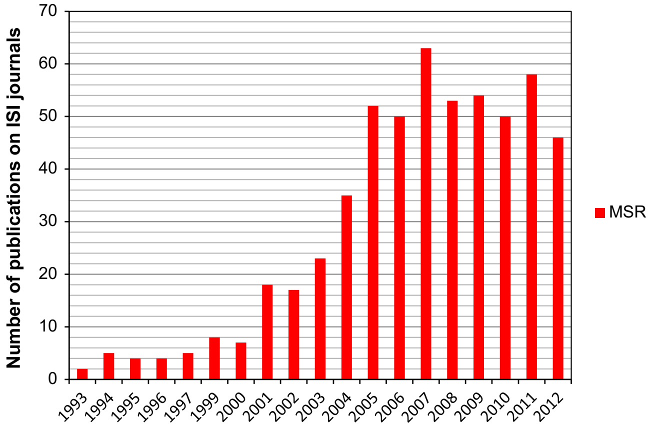


Fig. 4. Number of publications on ISI journals vs years about MSR reaction (Scopus database: www.scopus.com).

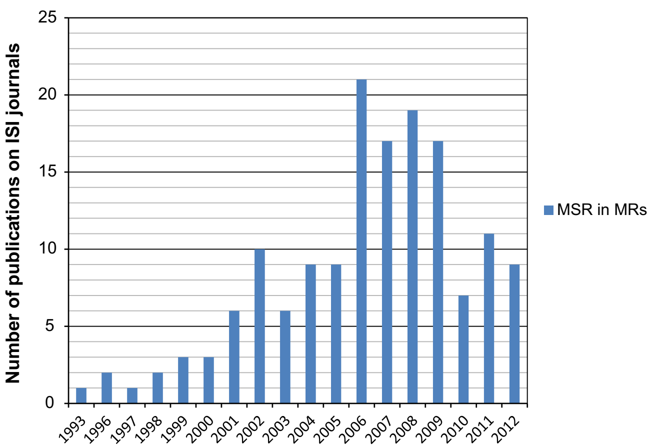


Fig. 5. Number of publications on ISI journals vs years about MSR reaction in MRs (Scopus database: www.scopus.com).

conditions, whereas high costs, fuel crossover, loss of performances at $T > 100$ °C are the main Nafion drawbacks [102]. PEMFCs are fueled by pure hydrogen and the CO tolerance for $T \leq 80$ °C is of a few ppm. As a consequence, much scientific attention has been devoted to improve the catalyst tolerance to CO, pointing out that Pt/Ru alloys are the most promising [103]. However, in the field of high-temperature (HT) PEMFCs, Nafion does not offer the best performances due to the reduced hydration conditions. Therefore, other kinds of polymers are useful as polymer electrolyte membranes instead of Nafion. Among them, hybrid polymeric membranes based on blend of, for example, sulfonated poly-ether-ether-ketone (S-PEEK) and poly-benzimidazole (PBI) or S-PEEK derivative membranes such as sulfonated poly-ether-ether-ketone with cardo group (S-PEEK-WC) offer good performances in terms of proton conductivity and resistance to fuel crossover in the temperature range of 80–200 °C [104]. Furthermore, in the field of HT-PEMFCs, CO tolerance of the anodic catalyst is higher, around 20,000–30,000 ppm [103] and hydrogen does not need to be highly purified, reducing the processes (and consequent costs) useful for the hydrogen separation/purification.

5. Feasibility study of methanol steam reforming reaction via MRs

As reported in Fig. 4, the number of publications on ISI journals regarding MSR reaction as a main topic is depicted during the years, whereas the number of publications about the combination between MSR reaction and MRs is shown in Fig. 5. It is quite evident that, in both figures, the interest towards this kind of reaction is grown even though membrane-based methanol reforming systems have been studied by a number of academic and industrial organizations only as a particular field of a general interest on MSR reaction [38].

However, MRs offer various benefits over low-pressure systems for hydrogen production combined with catalytic CO mitigation even though they also show various drawbacks, particularly the fragile nature of thin metal foils and the high cost.

Table 2
Some of the most representative experimental results about MSR reaction in MRs from the open literature.

Membrane	Membrane preparation	H_2/N_2 selectivity	Catalyst	H_2O/ CH_3OH	GHSV [h^{-1}]	T [°C]	p [bar]	Conv. [%]	H_2 recovery [%]	H_2 permeate purity [%]	Ref.
Pd–Ag (3.9 mm layer)/ a-Al_2O_3	ELP	Infinite	$CuO/ZnO/Al_2O_3$	1/1	600[a]	250	3	100	45	≈ 100	[105]
							10		95		
Pd–Ag (20–25 mm layer)/PSS	ELP	–	$CuO/ZnO/Al_2O_3$	1.2/1	5[b]	240	10	36,1	18	–	[106]
Carbon molecular sieve	Pyrolysis	62[c]	$CuO/ZnO/Al_2O_3$	4/1	–	200	1	≈ 95	≈ 84	–	[107]
SiO_2/g-Al_2O_3/Pt-SiO_2/PSS	Soaking-rolling	–	Cu–Zn/based	1.3/1	–	230	–	100	9.1	–	[108]
Pd (20 mm layer)/PSS	ELP	4000	$Cu/ZnO/Al_2O_3$	1.2/1	10[b]	350	6	≈ 95	97	99.9	[109]
Pd–Ag/TiO_2-Al_2O_3	ELP	–	Ru–Al_2O_3	4.5/1	–	550	1.3	65	–	≈ 72	[110]
SiO_2/g–Al_2O_3	Soaking-rolling	≈ 37	Cu-Zn/based	3/1	–	260	–	42	5	98	[111]
Carbon-supported	Pyrolysis	≈ 5.5	CuO/Al_2O_3/ ZnOMgO	3/1	–	250	2	55	–	≈ 80	[112]
Carbon-supported	–	–	$Cu/ZnO/Al_2O_3$	1.5/1	1[b]	250	2	≈ 99	–	97	[113]
Pd (20–25 mm layer)/PSS	ELP	Infinite	Cu-based	1.2/1	–	350	–	99	–	≈ 100	[117]
Dense Pd–Ag (50 mm thickness)	Cold-rolling	Infinite	CuO/Al_2O_3/ ZnOMgO	3/1	≈ 0.4	300	3	–	80	≈ 100	[114]
Dense Pd–Ru–In (200 mm thickness)	–	Infinite	$Cu/ZnO/Al_2O_3$	1.2/1	–	200	7	≈ 90	≈ 24	≈ 100	[115]
Dense Pd–Cu (25 mm thickness)	–	Infinite	Cu–Zn based	–	–	300	10	> 90	≈ 38	≈ 100	[11]

[a] [sccm/h/g-cat).
[b] WHSV.
[c] H_2/Ar selectivity.

In particular, the cost of palladium represents a potential barrier for membrane-based systems to enter in the market. Therefore, being the palladium intrinsically expensive, there has been in the last years a crucial need to operate in MRs with thin supported palladium membranes instead of dense self-supported foils and much progress has been made in this area. Nowadays, most of the methanol reforming units have been represented by MRs, mainly for the advantageous reasons listed above and in spite of their higher cost. In Table 2, the most representative results in terms of conversion, hydrogen recovery and so on are reported about MSR reaction performed in MRs. In detail, this table summarizes the different typology of membranes used in MRs for conducting MSR reaction besides the type of catalyst used and other important parameters such as: H_2/N_2 ideal selectivity, H_2O/MeOH feed ratio, reaction pressure, reaction temperature, etc.

In particular, Table 2 points out that in the last years many efforts have been made towards the development of composite Pd-based membranes (a dense layer of Pd deposited onto a porous support) and not Pd-based MSR membrane-based systems. Nevertheless, some data from literature are also given about the utilization of dense, self-supported Pd-based membranes in order to offer a more complete view on the topic. This table shows how, by reducing the amount of palladium (in membranes constituted by few microns of palladium layer deposited on porous supports), in some case [105] it is possible to maintain the full H_2/other gas selectivity like the dense one [114,115] with high performances in terms of methanol conversion and hydrogen recovery. However, this table reports the most recent findings in this area referring to composite Pd-based MRs for performing MSR reaction. More in detail, one of the most significant developments in the area is represented by the study of Israni and Harold [105], who synthesized a thin Pd–Ag layer (3.9 μm) deposited via electroless plating deposition (ELP) onto a porous α-Al_2O_3 support. This membrane shows a full H_2/N_2 perm-selectivity and allows to reach complete methanol conversion during MSR reaction at 250 °C with a hydrogen recovery varying from 45 to 95%, depending on the reaction pressure in the range of 3–10 bar. In this case, the purity of the hydrogen permeated stream was 100%. Also Lin and Rei [109] prepared a supported Pd layer (20 μm) onto a porous stainless steel (PSS) support with a H_2/N_2 perm-selectivity of around 4000, useful for obtaining 95% of methanol conversion with a hydrogen recovery of around 97% and a hydrogen permeate purity of 99.9% at 6 bar and 350 °C. In other cases, the Pd-based composite membranes did not give great results, probably because the presence of defects in the Pd-layer affected the H_2 perm-selectivity with respect to all the other gases with a consequent loss of performances in terms of conversion (due to a lower "shift effect"), hydrogen recovery and purity. Table 2 also shows new findings on not Pd-based MRs, namely carbon and silica-based membranes [107,108,111–113]. In the study of Mendes and co-workers [117], the carbon membrane from Carbon Membranes Ltd. is developed via pyrolysis method of dense cellulose cupra-amonia hollow fibres and possesses relatively low H_2/N_2 perm-selectivity, even if it allows to reach methanol conversion higher than 90% with a hydrogen recovery > 80%. On the contrary, Briceño et al. [116] prepared the supported carbon membrane based on a porous ceramic support of TiO_2 coated with ZrO_2, onto which various polymeric solutions as carbon precursors have been deposited and, then, pyrolysed. The supported carbon membrane was useful for obtaining a conversion higher than 50% and a hydrogen permeate purity of around 80% [112].

In the same field, Zhang et al. [113] used a carbon-based MR to carry out MSR reaction. The carbon membrane was used as a 6-mm i.d. tube with a wall thickness of 20–3 μm and sealed inside a stainless steel tube. As expected, methanol conversion equal to almost 100% was reached in the carbon-based MR and it resulted, as expected, higher than the conventional fixed-bed reactor in the temperature range of 200–250 °C. Furthermore, the hydrogen permeate purity was found around 97%.

Lee's group [108,111] used both supported SiO_2/γ-Al_2O_3/Pt-SiO_2/PSS and SiO_2/γ-Al_2O_3 membranes achieving different results depending on the kind of membrane used in the MR. The first membrane was useful for achieving complete methanol conversion even though the hydrogen recovery was quite low (< 10%). On the contrary, during the MSR reaction the second membrane was able to give in the MR more than 40% of methanol conversion, a poor hydrogen recovery but a quite interesting hydrogen purity in the permeate (98%).

The reported experimental data in Table 2 about the application of dense self-supported Pd-based membranes [114,115] show great results in terms of complete conversion, high hydrogen recovery and almost 100% hydrogen permeate purity, even if in these studies the issue about the need of decreasing the palladium thickness is not discussed. In particular, Basile's group spent much attention in the last years to carry out MSR reaction in inorganic MRs [110,114,120–123]. They compared MRs and conventional fixed-bed reactors by investigating such parameters as reaction temperature and pressure, time factor (residence time), H_2O/MeOH feed molar ratio, sweep gas flow rate and its modality configuration (co-current and counter-current) with respect to the feed and oxygen addition (in the oxidative MSR reaction [123]). Various membranes, both dense and composite, in tubular and sheet shape, have been used during the experimental tests of Basile and co-workers such as tubular dense self-supported Pd_{77}–Ag_{23} with a thickness of 50 μm produced at ENEA Laboratory (Italy), dense Pd_{80}–Ag_{20} sheet with a thickness of 60 μm produced at Laboratory of Noble Metals of Institute of Metallurgy (RAS), tubular composite Pd–Ag/TiO_2–Al_2O_3 produced at CNR-ICCOM Laboratory (Italy), tubular composite Pd–Ag on asymmetric ceramic support produced at University of Genova Laboratory (Italy) and silica membranes from Department of Chemical Engineering, Nanostructure Material Research Center, Sahand University of Technology, Tabriz (Iran). At any given condition, Basile and co-workers demonstrated that the MRs show superior performances to the CRs, operating at the same experimental conditions in terms of methanol conversion, selectivity and productivity, all of which are driven by the constant removal of hydrogen from the reactor zone.

However, other interesting studies are present in the open literature and they are related to the need of new findings, particularly oriented to prepare and use supported Pd-based membranes to carry out MSR reaction. For example, Lin's group [117] used supported PSS Pd-membranes supplied by Worcester Polytechnic Institute, in which the Pd-layer (20–25 μm) was electroplated onto the support. They performed MSR reaction at 350 °C and with a H_2O/MeOH feed ratio of 1.2/1, using a Cu-based catalyst reaching conversion higher than 99% and with a pure hydrogen recovery in the permeate side. Lin et al. theorized that a reverse spillover mechanism is responsible for the improved reaction rates obtained in Pd membrane reactors containing Cu-based catalysts. Practically, they supposed that the formed hydrogen from the reforming reaction is able to migrate directly from the active Cu-based catalyst site to the Pd membrane surface.

Han et al. [7] prepared a dense self-supported Pd–Cu membrane with 25 μm thickness in order to carry out MSR reaction and supply a 3-kW PEMFC. Complete conversion and hydrogen recovery with a purity of 99.9999% are the main performances of this MR. Successively, Han et al. [118,119] used a new generation of this kind of MRs for a nominal 25-kW unit operating at 70–75% recovery. The device was planned to be used in a PEM stack (Hyundai Motors) and to integrate it a hybrid vehicle.

Other important researchers like Wieland et al. [11] carried out MSR reaction in MRs by studying three different dense and self-supported Pd-alloy membranes, Pd–Ag, Pd–Cu and Pd–V–Pd.

Among them, Wieland′s group demonstrated that Pd–V–Pd membrane (40 μm as a thickness) possesses high permeation rates, but it is not stable and suffers mechanical cracks at pressure higher than 6 bar. Pd–Cu membrane (25 μm as a thickness) was found to be much more stable, but with lower hydrogen permeation with respect to the third Pd–Ag membrane (40 μm of thickness). Furthermore, they pointed out that the presence of CO or methanol may significantly affect the hydrogen permeating flux through the membrane because these components compete with the adsorption of hydrogen, decreasing its permeating flux by up to 70%. However, Wieland′s group found that, by using MRs housing Pd–Cu and Pd–Ag membranes for the MSR reaction, at $T=300$ °C the conversion is higher than 99% at pressures higher than 5 bar and it overcomes the equilibrium conversion of a correspondent conventional reactor at pressures > 20 bar.

Furthermore, Fig. 6 shows a comparison in terms of methanol conversion versus reaction temperature among the last 5 years literature data for MSR performed in both CRs and MRs.

A direct comparison among all the experimental data from literature reported in this figure is not possible owing to the different operating conditions adopted by each author. Nevertheless, from a qualitative point of view it is possible to observe that most of the methanol conversions from the reported data about MRs is concentrated between 200 and 300 °C and their values are not lower than 50%. On the contrary, most of the methanol conversions from CRs higher than 50% are reported in the temperature range from 300 to 400 °C. This aspect depicts to the reader a scenario in which great methanol conversions are achievable from both CRs and MRs. Nevertheless, MRs operate at lower reaction temperature than CRs with a consequent possible benefit in terms of energy saving. Furthermore, as another benefit MRs may collect a purified hydrogen stream in the permeate side with a concentration depending on which kind of membrane is utilized. Furthermore, another important issue is represented by the concentration of CO in the hydrogen rich-stream produced via MSR reaction for PEMFCs supply. As stated in the first part of this review, the CO concentration tolerance of such a PEMFC depends on its operating temperature. In Table 3, some recent experimental results from literature concerning CO concentration in the MSR reformed stream of CRs [103,131,134–137] and both permeate and retentate streams of MRs are shown. As well known, low-temperature (LT)-PEMFCs work at $T<100$ °C (commonly ≈ 80 °C) and the CO tolerance for the supplied hydrogen stream is

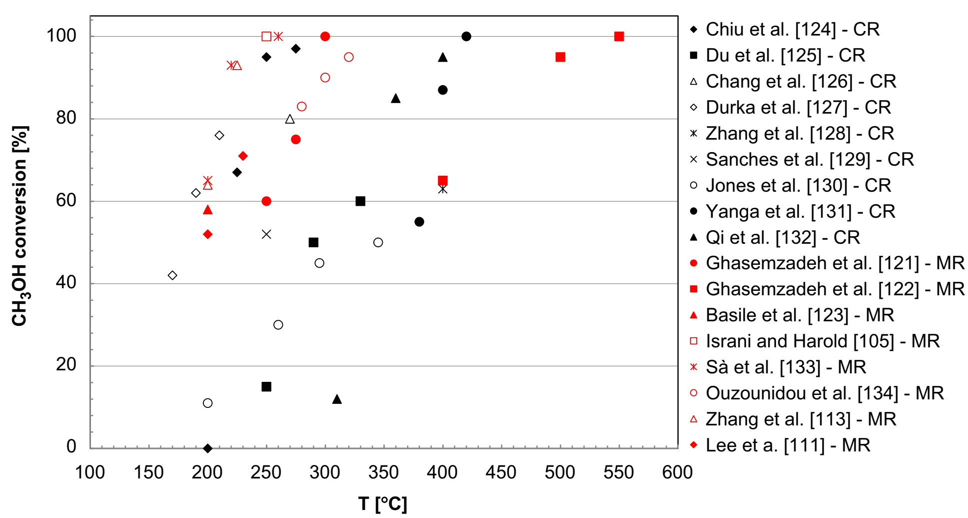


Fig. 6. Methanol conversion vs reaction temperature for MSR reaction: comparison among literature data for both CRs and MRs [124-130,132,133].

Table 3
Literature data about CO level in the reformed stream of some CRs and in both permeate and retentate streams of some MRs.

MRs						
T **[°C]**	***p*** **[bar]**	**Catalyst**	**Membrane**	**CO level in the permeate side [ppm]**	**CO level in the retentate side [ppm]**	**Ref.**
230	–	$Pt/SiO_2–Cu/Zn$	$SiO_2/g-Al_2O_3/Pt-SiO_2/PSS$	90–120	4600[b]	Lee et al. [111]
200	1	$CuO/ZnO/Al_2O_3$	Carbon molecular sieve	< 20	–	Sà et al. [107]
350	6	$Cu/ZnO/Al_2O_3$	Composite Pd/PSS	n.d.	60000[a]	Lin and Rei [109]
–	–	–	–	< 1	30000[b]	Han et al. [119]
350	6	Cu-based	Composite Pd/PSS	n.d.	47000[b]	Lin et al. [117]
250	5	$CuO/ZnO/Al_2O_3$	dense self-supported Pd–Ag	< 10	1000[b]	Israni and Harold [105]
300	3,5	$CuO/Al_2O_3/ZnO/MgO$	dense self-supported Pd–Ag	< 10	–	Iulianelli et al. [120]
CRs						
T **[°C]**	***p*** **[bar]**	**Catalyst**		**CO level in the reformed stream [ppm]**		**Ref.**
200	1	CuO–MnO		71		Ouzounidou et al. [134]
180	1	$CuO/ZnO/Al_2O_3$		500[b]		Pan et al. [103]
420	1	ZnO/Al_2O_3		≈ 7400[b]		Yang et al. [131]
300	1	$Cu/ZnO/Al_2O_3$		≈ 8000[b]		Patel et al. [135]
250	1	$Cu/ZnO/Al_2O_3$		≈ 1000[b]		Purnama et al. [136]
250	1	Cu/ZrO_2		≈ 100[b]		Ritskopf et al. [137]

lower than 20 ppm. Therefore, as shortly resumed in Table 3, the CO level of the reformed streams coming from CRs are not adequate to directly supply LT-PEMFCs, needing further separation/purification of the hydrogen rich-streams. On the contrary, the reformed stream can be useful for HT-PEMFCs, being the CO level lower than 20,000 ppm and, then, in accordance with the HT-PEMFCs CO tolerance requirements [103]. Concerning MRs, as shown in Table 3, the CO level in the permeate streams depends on the kind of membrane housed inside the MR. So, dense self-supported Pd-based membranes allow high purity of permeated hydrogen and, as a consequence, low CO level ($<$ 10 ppm), making possible the hydrogen supply to LT-PEMFCs.

Unfortunately, the great values of low CO concentration of the permeated hydrogen of dense Pd-based membranes are in contrast with the cost its-self of the membranes. Therefore, many researchers are involved to find a compromise between high purity permeated hydrogen and dense Pd-based membrane cost. However, in some case the retentate stream of such MRs shows CO concentrations lower than 20,000–30,000 ppm, usually recognized as a set tolerance for HT-PEMFCs [103]. In that case, both the permeate and retentate streams could be useful for LT-PEMFCs and HT-PEMFCs supply, respectively.

6. MSR-FC integration

As above introduced, fuel cells are very efficient for converting chemical into electric energy and hydrogen is the ideal fuel for this application. However, hydrogen has low energy density making it difficult to store and transport. Furthermore, an entirely new distribution infrastructure and storage is needed [138]. Previous reasons directed the scientific community to search for new energy vectors and methanol demonstrated to be good alternative [138]. In fact, it has higher energy density than hydrogen, it is easier to handle and store and, especially, it shows relatively low reforming temperature (240–260 °C) due to absence of C–C bonds. As a result, many authors have been studying the MSR for in situ hydrogen production to feed fuel cells. Commercial power supplies are already available combining in situ hydrogen generation by MSR to supply high temperature fuel cells, namely by Ultracell [139], AixCellSys [140] and Serenergy [141]. The fuel cell and the reformer upon the closeness can be defined as external reforming (the MSR operated as standalone system) or internal reforming (the MSR is part of the fuel cell stack) [142].

6.1. External reforming

Methanol steam reforming for in situ hydrogen production for fuel cell applications has been studied mostly as a stand-alone process. An external reformer system consists of a combustor where a small fraction of fuel is burned and provides heat for the following steps, a vaporizer to heat and vaporize the fuel, a reformer to carry out the reforming reaction and a carbon monoxide converter to carbon dioxide such as a *preferential oxidation* (PROX) reactor (Fig. 7). Hydrogen purification can be achieved by *pressure swing adsorption* (PSA) or metal membrane processes.

AixCellSys [140,143] and Serenergy [141] used similar strategies to produce power supplies that combine external reforming and HT-PEMFC. These systems integrate a combustor, which burns the non-reacted hydrogen from the fuel cell out-stream, a vaporizer to heat and vaporize the fuel (water/methanol molar ratio of 1.5:1), a reformer loaded with $CuO/ZnO/Al_2O_3$ and HT-PEMFC (Fig. 8). These power supplies do not require CO removal due to the high CO tolerance of HT-PEMFC, up to ca. 1% for fuel cells operating at 170 °C or above [144]. The start-up period is slightly longer for HT-PEMFC systems (5–15 min) due to the acid nature

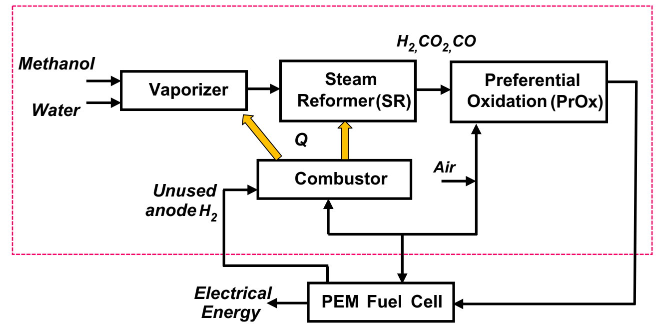


Fig. 7. Standard setup for external reforming (adapted from [78]).

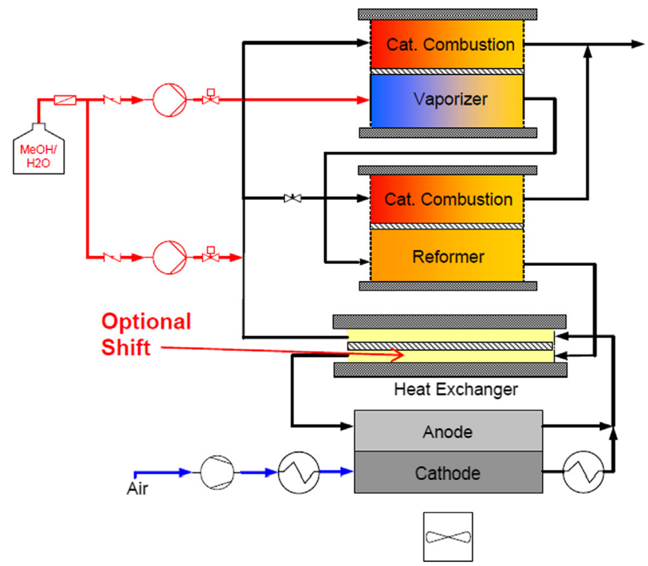


Fig. 8. Integrated MSR-FC, (adapted from [143]).

of polymeric membranes (polybenzimidazole—PBI) that requires materials suitable for operating under corrosive conditions, increasing the size of the fuel cell stack [145,146]. During the start-up period, a lithium battery provides the energy for two heaters until the operation temperature is reached. Both systems are compact and represent an important step towards the commercialization of power supplies based on MSR/FC systems. However, the maximum electric power output is 0.2 W cm^{-2} for both systems [143], which is half of the performance for a fuel cell fed with pure hydrogen.

Power supplies combining low temperature PEMFC and MSR are also described in literature and commercially available. H_2 planet offers a power supply with this technology [145] and Honda proposed a prototype of a car equipped with a MSR-LT-PEMFC [147]. The International Organization for Standardization (ISO 14687) recommends for road vehicles application a maximum CO concentration of 0.2 ppm for feeding LT-PEMFC [148], which requires the reformate deep purification. This is conventionally achieved coupling to the MSR-CRs a WGS and a PROX reactors [149], even though palladium membranes being considered with great advantages.

CO_2 does not affect poison the fuel cell catalyst like CO, since dilutes further the hydrogen originating losses of ca. 20% in the maximum power density [149]. CO_2 concentration increases as the reformate stream progresses inside the fuel cell up to a point where fuel starvation occurs. This fuel starvation normally happens well before the maximum power density when pure hydrogen is supplied. To partially compensate this drawback, a high feed

flow rate is supplied that originates a significant hydrogen waste of ca. 30% [149].

The external integration simplifies the addition of new components to the system that can improve the process overall efficiency. As previously mentioned, an ideal reformer should produce a hydrogen stream, mostly free of CO, and containing low concentrations of CO_2, methanol and water. This can be achieved using a Pd-based reformer that allows the selective removal of hydrogen from the reaction medium [7]. As previously reported in the text, besides originating a hydrogen pure stream, a Pd-based MR allows improving the methanol conversion since hydrogen product is selectively removed and the backward reaction is prevented [150]. Though very attractive, hydrogen permeates the membrane if a very low hydrogen partial pressure is maintained in the permeate side, which can be costly. Instead of selectively removing hydrogen, CO_2 removal could be considered and, since CO_2 concentration in air is quite low, ca. 400 ppm, its use as sweep gas would provide an effective low cost permeation driving force. For fuel cells with low sensitivity towards CO such as HT-PEMFC, carbon dioxide removal would be the best. However, there is still no CO_2 selective membrane that can operate at reforming temperatures through recent efforts [148,151,152]. Alternatively, the use of adsorbents such as zeolite 13X [153] and hydrocalcites [154] are referred in the literature as being able to remove selectively carbon dioxide from the reaction medium or from the reformate stream. However, after saturation the regeneration step is difficult to accomplish. A thermal swing adsorption (TSA) process could in principle be considered for purifying the reformate stream but this is normally an energy demanding process [155].

The thermal resistance between the heat source and catalyst bed must be as small as possible. For external reforming integration the heat required for the reforming process is typically provided by a combustor [4,157]. The flow and heat transfer (combustor–reformer) effect on the reactor performance has been studied using phenomenological models [156,158,159]. Heat conduction through the microreactors walls was observed to have a significant impact on the temperature distribution and consequently on the methanol conversion [160]. Thus, to optimize the heat transfer high conductive materials should be used on combustor and reformer fabrication. The heat transfer is also affected by different designs adopted for combustors and reformers. For example, by changing reformer and combustor from parallel channel design to serpentine, the flow velocity increases and, then, the stagnant film adjacent to the wall becomes thinner and the heat transfer coefficient increases [156,158]. A more efficient heat transfer from the combustor to the reformer allows higher hydrogen yields. In small devices the heat management is critical because the high surface-to-volume ratio. A cylindrical design organized in a "thermal cascade" can be adopted to minimize the heat losses, having cooler layers covering hotter ones, thus the combustor is inserted in the center followed by the vaporizer, the reformer and so on [161,162].

External reforming has the advantage of being not restricted to a reformer/fuel cell stack configuration, allowing different designs potentially more efficient for fuel processing. The reformer can operate at higher temperatures and a MR configuration can be used, which results in higher conversions and the production of a purified hydrogen stream.

6.2. Internal reforming

Internal reforming involves heat and mass exchange between the MSR and electrochemical reaction and it is classified as direct or indirect, depending on the MSR catalyst if inserted or not in the anode compartment, respectively [142].

Fuel cells are exothermic devices that waste ca. 50% of the input chemical energy as heat, while methanol steam reformers are endothermic; internal reforming targets to take advantage of efficient

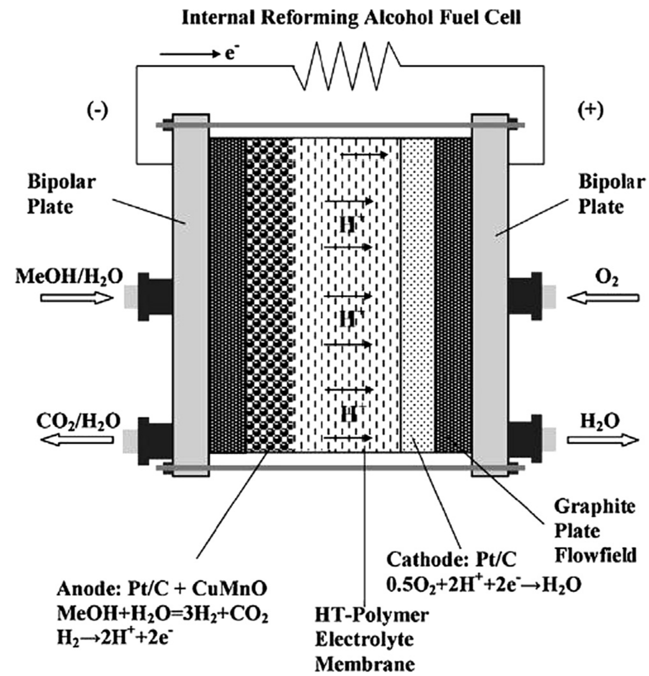


Fig. 9. Direct Internal MSR (adapted from [166]).

heat exchange between the two devices. LT-PEMFCs operate at ca. 80 °C and HT-PEMFCs at ca. 180 °C, while MSR operates at ca. 250 °C. Due to this mismatching operating temperature, many authors choose external reforming, but for HT-PEMFC a synergetic heat integration can be achieved if possible either or both to increase the fuel cell operating temperature or lower the reforming temperature. Since the operation of HT-PEMFC is limited to a maximum operating temperature of 200 °C, a few authors proposed lowering the reforming temperature [37,103,163]. At 180 °C the methanol conversion in a commercial catalyst ($CuO/ZnO/Al_2O_3$) is very low. For example, for a contact time of $W_{cat}/F_{MeOH}=30$ kg s mol^{-1} the methanol conversion is 80% at 250 °C and 13% at 180 °C [164]. Pan et al. [103] were as first authors to study the performance of an indirect internal reforming coupled with a HT-PEMFC operating at 180–200 °C. They loaded the reformer with 149 g of commercial catalyst ($CuO/ZnO/Al_2O_3$) and obtained a hydrogen yield of 400 dm^3 h^{-1} kg$_{catalyst}$$^{-1}$ for nearly 100% of methanol conversion. The fuel cell stack exhibited a lower maximum power density when fed with reformate compared to when fed with pure hydrogen but a higher energy efficiency [103].

Avgouropoulos et al. [165,166] used a fuel cell equipped with a PBI electrolyte membrane by ADVENT TPS that resists to higher temperatures, up to 210 °C, and a methanol reforming catalyst of $CuMnO_x$ loaded in the anode chamber (Fig. 9). The system was operated at 200–210 °C producing a current density of 0.17 A cm^{-2} at 600 mV. The advantages of the indirect internal reforming are compactness and heat integration. The reforming conversion is also enhanced by the continuous electrochemical hydrogen removal from the reforming reaction medium. However, since PBI membranes are intolerant to high methanol concentrations, resulting in low power output [36,167].

7. Perspectives

The production of MSR reaction still continues to be an active area of research and much progress has been achieved both in the field of catalysts development and applications involving both CRs

and MRs, even though many problems still remain to be solved. This review deals with MSR reaction to produce hydrogen for PEMFC supply combined to an overview on the new findings on MSR catalyst development and inorganic MR technology. In particular, it is reasonable to understand that the exploitation of renewable sources such as methanol constitutes an important possibility in the route of hydrogen production via reforming reactions by inorganic MR technology. This combination could drive to an improvement of the hydrogen production units, making possible the requirements for the integration of methanol-based fuel processors with PEM fuel cells. A critic issue not largely addressed in the specialized literature involves this concept: considering that natural gas and, more in general, other derived fossil fuels are essentially utilized for stationary applications, it is expected that alcohols such as methanol could have a major impact on the future portable applications. However, reactor and system development activities by several scientific groups around the world demonstrated the ability of performing MSR reaction at small and large scale and at high efficiencies. As a consequence, selection of material and system design vary a lot from the very small metal, glass or ceramic micro-reactors to the large scale, high pressure membrane-based systems. In the area of inorganic MRs applied to MSR reaction, a relevant still unsolved issue is represented by the impossibility of comparing the performances (in terms of conversion, hydrogen yield and hydrogen recovery) among the existing scientific works owing to the different operating conditions adopted by each author during the experimental tests. Furthermore, even though in literature there are a number of studies on MSR reaction performed in MRs, no one of them focuses on cost analysis of these devices. This aspect points out that inorganic MR technology still presents some deficiencies to be overcome before its implementation at larger scales. As a future perspective, a new research approach should be aimed by the preparation of composite membranes based on very thin Pd-layer deposited onto porous supports showing very high hydrogen/other gas perm-selectivity, able to operate for long periods at high temperatures and pressures as well as to develop membrane systems not based on palladium by exploiting the potentiality of HT-PEMFCs to tolerate higher level of CO in the hydrogen stream supplied.

8. Conclusions

Major advances have been made in the field of hydrogen production through MSR. New catalyst base on cooper or/and palladium are being developed and is expected higher catalytic activity, making possible the complete integration of MSR-reactors with PEMFC. Tubular reactors or coil designs cause high pressure drops and are not the most suitable for MSR reaction, others designs as radial demonstrate being more appropriate. MRs play an important role in hydrogen production, promising weight and space savings. Dense metal membranes provide high purity hydrogen over a wide range of pressure and temperature. The selective removal of hydrogen enhances the methanol conversion that is higher than the conversion in a conventional reactor. But the futures of membrane reactors for fuel cell depends on the ability to produce high permeate fluxes at low system pressure with moderate cost and suitable stability in all phases of a typical load cycle.

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References

[1] Wee J. Applications of proton exchange membrane fuel cell systems. Renewable & Sustainable Energy Reviews 2007;11:1720–38.
[2] Bose S, Kuila T, Nguyen TXH. Polymer membranes for high temperature proton exchange membrane fuel cell: recent advances and challenges. Progress in Polymer Science 2011;36:813–43.
[3] Heinzel A, Vogel B, Hiugner P. Reforming of natural gas hydrogen generation for small scale stationary fuel cell systems. Journal of Power Sources 2002;105:202–7.
[4] Chein RY, Chen YC, Lin YS, Chung JN. Hydrogen production using integrated methanol-steam reforming reactor with various reformer designs for PEM fuel cells. International Journal of Hydrogen Energy 2012;36:466–76.
[5] Pettersson LJ, Westerholn R. State of the art of multi-fuel reformers for fuel cell vehicles: problem identification and research needs. International Journal of Hydrogen Energy 2001;26:243–64.
[6] Lindström B, Pettersson LJ. Development of a methanol fuelled reformer for fuel cell applications. Journal of Power Sources 2003;118:71–8.
[7] Han J, Kim IS, Choi KS. Purifier-integrated methanol reformer for fuel cell vehicles. Journal of Power Sources 2000;86:223–7.
[8] Lu GQ, Diniz de Costa JC, Duke M, Giessler S, Socolow R, Williams RH, et al. Inorganic membranes for hydrogen production and purification: a critical review and perspective. Journal of Colloid and Interface Science 2007;314:589–603.
[9] Xiu S, Shahbazi A. Bio-oil production and upgrading research: a review. International Journal of Hydrogen Energy 2012;16:4406–14.
[10] Basile, A, Iulianelli, A, Longo, T, Liguori, S, De Falco, M. Pd-based selective membrane State-of-the-Art. In: Membrane reactors for hydrogen production processes, L Marrelli, M De Falco & G Iaquaniello, editors, Springer London Dordrecht Heidelberg New York; 2011 Chapter 2, pp. 21–55, ISBN 978-0-85729-150-9, http://dx.doi.org/10.1007/978-0-85729-151-6.
[11] Wieland S, Melin T, Lamm A. Membrane reactors for hydrogen production. Chemical Engineering Science 2002;57:1571–6.
[12] Damle AS. Hydrogen production by reforming of liquid hydrocarbons in a membrane reactor for portable power generation—experimental studies. Journal of Power Sources 2009;186:167–77.
[13] Iulianelli, A, Liguori, S, Longo, T, Basile, A. Inorganic membrane and membrane reactor technologies for hydrogen production. in: Hydrogen production: prospects and processes, Damon Robert Honery and Patrick Moriarty, editors, Victoria, Australia, Nova Science Publishers, Series: Energy Science, Engineering and Technology, isbn:978-1-62100-246-8; 2012. Chapter 12, pp. 377–398.
[14] Basile A. Hydrogen production using Pd-based membrane reactors for fuel cells. Topics in Catalysis 2008;51:107–22.
[15] Lin YM, Rei MH. Process development for generating high purity hydrogen by using supported palladium membrane reactor as steam reformer. International Journal of Hydrogen Energy 2000;25:211–9.
[16] Mallada R, Menéndez M. Inorganic membranes: synthesis, characterization and applications. Technology & Engineering 2008:460.
[17] Saracco G, Specchia V. Catalytic inorganic membrane reactors: present experience and future opportunities. Catalysis Reviews-science and Engineering 1994;36:305–84.
[18] Shu J, Grandjean BPA, Van Neste A, Kaliaguine S. Catalytic palladium-based membrane reactors: a review. The Canadian Journal of Chemical Engineering 1991;69:1036–60.
[19] Grashoff GJ, Pilkington CE, Corti CW. The purification of hydrogen—a review of the technology emphasizing, the current status of palladium membrane diffusion. Platinum Metals Review 1983;27:157–68.
[20] Hsieh HP. Inorganic membrane reactors—a review. AIChE Symposium Series 1989;85:53–67.
[21] Tong J, Shirai R, Kashima Y, Matsumura Y. Preparation of a pinhole-free Pd–Ag membrane on a porous metal support for pure hydrogen separation. Journal of Membrane Science 2005;260:84–9.
[22] Adhikari S, Fernand S. Hydrogen membrane separation techniques. Industrial & Engineering Chemistry Research 2006;45:875–81.
[23] Arstad B, Venvik H, Klette H, Walmsley JC, Tucho WM, Holmestad R, et al. Studies of self-supported 1.6 μm Pd/23 wt% Ag membranes during and after hydrogen production in a catalytic membrane reactor. Catalysis Today 2006;118:63–72.
[24] Dolan MD, Dave NC, Ilyushechkin AY, Morpeth LD, McLennan KG. Composition and operation of hydrogen-selective amorphous alloy membranes. Journal of Membrane Science. 2006;285:30–55.
[25] Falconer JL, Noble RD, Sperry DP. Catalytic membrane reactors. In: Noble RD, Stern SA, editors. Membrane separations technology: principles and applications. Elsevier; 1995. p. 669–712.
[26] Sà S, Sousa JM, Mendes A. Methanol steam reforming in a dual-bed membrane reactor for producing PEMFC grade hydrogen. Catalysis Today 2010;156:254–60.
[27] Agrell J, Birgersson H, Boutonnet M. Steam reforming of methanol over a $Cu/ZnO/Al_2O_3$ catalyst: a kinetic analysis and strategies for suppression of CO formation. Journal of Power Sources 2002;106(1–2):249–57.

[28] Jiang CJ, Trimm DL, Wainwright MS, Cant NW. Kinetic study of steam reforming of methanol over copper-based catalysts. Applied Catalysis A: General 1993;93(2):245–55.
[29] Jiang CJ, Trimm DL, Wainwright MS, Cant NW. Kinetic mechanism for the reaction between methanol and water over a Cu–ZnO–Al_2O_3 catalysts. Applied Catalysis A: General 1993;97(2):145–58.
[30] Schuessler M, Lamla O, Stefanovsky T, Klein C, zur Megede D. Autothermal reforming ofmethanol in an isothermal reactor—concept and realisation. Chemical Engineering & Technology 2001;24(11):1141–5.
[31] Takahashi T, Inoue M, Kai T. Effect of metal composition on hydrogen selectivity in steam reforming of methanol over catalysts prepared from amorphous alloys. Applied Catalysis A: General 2001;218:189–95.
[32] Sekizawa K, Yano S, Eguchi K, Arai H. Selective removal of CO in methanol reformed gas over Cu-supported mixed metal oxides. Applied Catalysis A: General 1998;169:291–7.
[33] Alejo L, Lago R, Peňa MA, Fierro JLG. Partial oxidation of methanol to produce hydrogen over Cu–Zn-based catalysts. Applied Catalysis A: General 1997;162: 281–97.
[34] Shen GC, Fujita S, Matsumoto S, Takezawa N. Steam reforming of methanol on binary Cu/ZnO catalysts: effect of preparation condition upon precursor, surface structure and catalytic activity. Journal of Molecular Catalysis A: Chemical 1997;124:123–36.
[35] Reitz TL, Ahmed S, Krumpelt M, Kumar R, Kung HH. Characterization of CuO/ZnO under oxidizing conditions for the oxidative methanol reforming reaction. Journal of Molecular Catalysis A: Chemical 2000;162:275–85.
[36] Velu S, Suzuki K, Kapoor MP, Ohashi F, Osaki T. Selective production of hydrogen for fuel cells via oxidative steam reforming of methanol over CuZnAl (Zr)-oxide catalysts. Applied Catalysis A: General 2001;213:47–63.
[37] Chein R-Y, Chen Y-C, Lin Y-S, Chung JN. Experimental study on the hydrogen production of integrated methanol-steam reforming reactors for PEM fuel cells. International Journal of Thermal Sciences 2011;50:1253–62.
[38] Palo D, Dagle R, Holladay J. Methanol steam reforming for hydrogen production. Chemical Reviews 2007;107:3992–4021.
[39] Turco M, Bagnasco G, Cammarano C, Senese P, Costantino U, Sisani M. Cu/ ZnO/Al_2O_3 catalysts for oxidative steam reforming of methanol: the role of Cu and the dispersing oxide matrix. Applied Catalysis B: Environmental 2007;77:46.
[40] Mastalir Á, Patzkó Á, Frank B, Schomäcker R, Ressler T, Schlögl R. Steam reforming of methanol over Cu/ZnO/Al_2O_3 modified with hydrotalcites. Catalysis Communications 2007;8:1684–90.
[41] Conant T, Karim A, Lebarbier V, Wang Y, Girgsdies F, Schlögl R, et al. Stability of bimetallic Pd–Zn catalysts for the steam reforming of methanol. Journal of Catalysis 2008;257:64–70.
[42] Jeong H, Kimb KI, Kimb TH, Ko CH, Park HC, Song IK. Hydrogen production by steam reforming of methanol in a micro- channel reactor coated with Cu/ ZnO/ZrO_2/Al_2O catalyst. Journal of Power Sources 2006;159:1296–9.
[43] Yong-Feng L, Xin-Fa D, Wei-Ming L. Effects of ZrO_2-promoter on catalytic performance of CuZnAlO catalysts for production of hydrogen by steam reforming of methanol,. International Journal of Hydrogen Energy 2004;29:1617–21.
[44] Ma L, Gong B, Tran T, Wainwright MS. Cr_2O_3 promoted skeletal Cu catalysts for the reactions of methanol steam reforming and water gas shift. Catalysis Today 2000;63:499–505.
[45] Clancy P, Breen J, Ross J. The preparation and properties of coprecipitated Cu–Zr–Y and Cu–Zr–La catalysts used for the steam reforming of methanol. Catalysis Today 2007;127:291–4.
[46] Shishido T, Yamamoto Y, Morioka H, Takaki K, Takehira K. Active Cu/ZnO and Cu/ ZnO/Al_2O_3 catalysts prepared by homogeneous precipitation method in steam reforming of methanol. Applied Catalysis A: General 2004;263:249–53.
[47] Jakdetchai O, Takayama N, Nakajima T. Activity enhancement of CuZn-impregnated Fsm-16 by modification with 1,3-butanediol for steam reforming of methanol. Kinetics and Catalysis 2005;46:56–64.
[48] Lindström B, Pettersson LJ, Menon PG. Activity and characterization of Cu/Zn, Cu/Cr and Cu/Zr on γ-alumina for methanol reforming for fuel cell vehicles. Applied Catalysis A: General 2002;234:111–25.
[49] Papavasiliou J, Avgouropoulos G, Ioannides T. Reforming of methanol over copper–manganese spinel oxide catalysts. Catalysis Communications 2005;6: 497–501.
[50] Oguchi H, Nishiguchi T, Matsumoto T, Kanai H, Utani K, Matsumura Y, et al. Steam reforming of methanol over Cu/CeO_2/ZrO_2 catalysts. Applied Catalysis A: General 2005;281:69–73.
[51] Liu Y, Hayakawa T, Tsunoda T, Suzuki K, Hamakawa S, Murata K, et al. Steam reforming of methanol over Cu/CeO_2 catalysts studied in comparison with Cu/ZnO and Cu/Zn(Al)O catalysts. Topics in Catalysis 2003;22:205–13.
[52] Agrell J, Birgersson H, Boutonnet M, Melián-Cabrera I, Navarro R, Fierro J. Production of hydrogen from methanol over Cu/ZnO catalysts promoted by ZrO_2 and Al_2O_3. Journal of Catalysis 2003;219:389–403.
[53] Liu Q, Wang L-C, Chen M, Liu Y-M, Cao Y, He H-Y, et al. Waste-free soft reactive grinding synthesis of high-surface-area copper–manganese spinel oxide catalysts highly effective for methanol steam reforming. Catalysis Letters 2008;121:144–50.
[54] Yao C-Z, Wang L-C, Liu Y-M, Wu G-S, Cao Y, Dai W-L, et al. Effect of preparation method on the hydrogen production from methanol steam reforming over binary Cu/ZrO_2 catalysts. Applied Catalysis A: General 2006;297:151–8.
[55] Marbán G, Valdés-Solís T, Fuertes AB. High surface area $CuMn_2O_4$ prepared by silica-aquagel confined co-precipitation. Characterization and testing in steam reforming of methanol. Catalysis Letters 2007;118:8–14.
[56] Yang H-M, Liao P-H. Preparation and activity of Cu/ZnO–CNTs nano-catalyst on steam reforming of methanol. Applied Catalysis A: General 2007;317:226–33.
[57] Gao L, Sun G, Kawi S. A study on methanol steam reforming to CO_2 and H_2 over the La_2CuO_4 nanofiber catalyst. Journal of Solid State Chemistry 2008;181:7–13.
[58] Iwasa N, Masuda S, Takezawa N. Steam reforming of methanol over Pd/ZnO: effect of the formation of PdZn alloys upon the reaction. Reaction Kinetics and Catalysis Letters 1995;55:349–53.
[59] Iwasa N, Mayanagi T, Masuda S, Takezawa N. Steam reforming of methanol over PdZn catalysts. Reaction Kinetics and Catalysis Letters 2000;69:355–60.
[60] Iwasa N, Kudo S, Takahashi H, Masuda S, Takezawa N. Highly selective supported Pd catalyst for steam reforming of methanol. Catalysis Letters 1993;19:211–6.
[61] Iwasa N, Mayanagi T, Nomura W, Arai M, Takezawa N. Effect of Zn addition to supported Pd catalyst in the steam reforming of methanol. Applied Catalysis A: General 2003;248:153–60.
[62] Chin YH, Wang Y, Dagle RA, Li XS. Methanol steam reforming over Pd/ZnO: catalyst preparation and pretreatment studies. Fuel Processing Technology 2003;83:193–201.
[63] Qi C, Amphlett JC, Peppley BA. Methanol steam reforming over NiAl and NiAl (Au, Rh, Ir)-layered double hydroxide derived catalysts. Catalysis Letters 2005;104:57–62.
[64] Karim A, Conant T, Datye A. The role of PdZn alloy formation and particle size on the selectivity for steam reforming of methanol. Journal of Catalysis 2006;243:420–7.
[65] Sá S, Silva H, Brandão L, Sousa J, Mendes A. Catalysts for methanol steam reforming—a review. Applied Catalysis B: Environmental 2010;99:43–57.
[66] Hessel V, Hardt S, Lowe H. Chemical micro processing engineering, fundamentals, modelling and reactions. Weinheim: Wiley-VCH, Verlag GmbH; 2004.
[67] Checchetto R, Bazzanella N, Patton B, Miotello A. Palladium membranes prepared by r.f. magnetron sputtering for hydrogen purification. Surface and Coatings Technology 2004;177–178:73–9.
[68] An H, Angli A, Agus B, Sasmito P, Jundika C, Kurnia A, et al. Computational fluid dynamics (CFD) analysis of micro-reactor performance: effect of various configurations. Chemical Engineering Science 2012;75:85–95.
[69] Jang J, Cheng C, Huang Y, Lee C, Leu C. Optimal design of parallel channel patterns in a micro methanol steam reformer. International Journal of Hydrogen Energy 2012;37:16974–85.
[70] Pattekar A, Kothare M. A microreactor for hydrogen production in micro fuel cell applications. Journal of Microelectromechanical Systems 2004;13:7–18.
[71] Telotte J, Kern J, Palanki S. Miniaturized methanol reformer for fuel cell powered mobile applications. International Journal of Chemical Reactor Engineering 2008;6:64.
[72] Karim A, Bravo J, Datye A. Non isothermally in packed bed reactors for steam reforming of methanol. Applied Catalysis A: General 2005;282:101–9.
[73] Perng S, Horng R, Ku H. Effects of reaction chamber geometry on the performance and heat/mass transport phenomenon for a cylindrical methanol steam reformer. Applied Energy 2012.
[74] Suh J, Lee M, Greif R, Costas P. Grigoropoulos, transport phenomena in a steam-methanol reforming microreactor with internal heating. International Journal of Hydrogen Energy 2009;34:314–22.
[75] Terazaki T, Nomura M, Takeyama K, Nakamura O, Yamamoto T. Development of multi-layered micro-reactor with methanol reformer for small PEMFC. Journal of Power Sources 2005;145:691–6.
[76] Kawamura Y, Ogura N, Yamamoto T, Igarashi A. A miniaturized methanol reformer with Si-based microreactor for a small PEMFC. Chemical Engineering Science 2006;61:1092–101.
[77] Oh S, Kim J. Method of catalyst coating in micro-reactors for methanol steam reforming. Applied Catalysis A: General 2007;316:83–9.
[78] Karim A, Bravo J, Gorm D, Conant T, Datye A. Comparison of wall-coated and packed-bed reactors for steam reforming of methanol. Catalysis Today 2005;110:86–91.
[79] Bravo J, Karim A, Conant T, Lopez G, Datye A. Wall coating of a CuO/ZnO/ Al_2O_3 methanol steam reforming catalyst for micro-channel reformers. Chemical Engineering Journal 2004;101:113–21.
[80] Lee M, Greif R, Costas P, Grigoropoulos H, Park F Hsu. Transport in packed-bed and wall-coated steam-methanol reformers. Journal of Power Sources 2007;166:194–201.
[81] Pan M, Wei X, Tang Y. Factors influencing methanol steam reforming inside the oriented linear copper fiber sintered felt. International Journal of Hydrogen Energy 2012;37:11157–66.
[82] Soria R. Overview on industrial membranes. Catalysis Today 1995;25(3–4):285–90.
[83] Westermann T, Melin T. Review – flow-through catalytic membrane reactors – Principles and applications. Chemical Engineering and Processing 2009;48:17–28.
[84] Lin YS. Microporous and dense inorganic membranes: current status and prospective. Separation and Purification Technology 2001;25:39–55.
[85] McLeary EE, Jansen JC, Kapteijn F. Zeolite based films, membranes and membrane reactors: progress and prospects. Mesopotamia & Mathematics Mesopotamia 2006;90:198–220.
[86] Fong YY, Abdullah AZ, Ahmad AL, Bhatia S. Review—development of functionalized zeolite membrane and its potential role as reactor combined

separator for para-xylene production from xylene isomers. Chemical Engineering Journal 2008;139:172–93.
[87] Huang J, El-Azzami LA, Ho WSW. Modeling of CO_2-selective water gas shift membrane reactor for fuel cell. Journal of Membrane Science 2005;261:67–75.
[88] Scholes CA, Smith KH, Kentish SE, Stevens GW. Review – CO_2 capture from pre-combustion processes – strategies for membrane gas separation. International Journal of Greenhouse Gas Control 2010;4:739–55.
[89] Andrić P, Meyer AS, Jensen PA, Johansen KD. Reactor design for minimizing product inhibition during enzymatic lignocellulose hydrolysis II. Quantification of inhibition and suitability of membrane reactors. Biotechnology Advances 2010;28:407–25.
[90] Reij MW, Keurentjes JTF, Hartmans S. Review—membrane bioreactors for waste gas treatment. Journal of Biotechnology 1998;59:155–67.
[91] Woodside SM, Bowen BD, Piret JM. Mammalian cell retention devices for stirred perfusion bioreactors. Cytotechnology 1998;28:163–75.
[92] Chatenet M, Dubau L, Job N, Maillard F. The (electro) catalyst membrane interface in the proton exchange membrane fuel cell: similarities and differences with non-electrochemical catalytic membrane reactors. Catalysis Today 2010;156:76–86.
[93] Mozia S. Photocatalytic membrane reactors (PMRs) in water and wastewater treatment: a review. Separation and Purification Technology 2010;73:71–91.
[94] Dittmeyer R, Höllein V, Daub K. Membrane reactors for hydrogenation and dehydrogenation processes based on supported palladium. Journal of Molecular Catalysis A: Chemical 2001;173(1–2):135–84.
[95] Saracco G, Neomagus HWJP, Versteeg GF, van Swaaij WPM. High-temperature membrane reactors: potential and problems. Chemical Engineering Science 1999;54:1997–2017.
[96] Coronas J, Santamaria J. Catalytic reactors based on porous ceramic membranes. Catalysis Today 1999;51:377–89.
[97] Edlund DJ, Pledger WA. Thermolysis of hydrogen sulfide in a metal-membrane reactor. Journal of Membrane Science 1993;77:255–64.
[98] Li A, Liang W, Hughes R. The effect of carbon monoxide and steam on the hydrogen permeability of a Pd/stainless steel membrane. Journal of Membrane Science 2000;165:135–41.
[99] Amandusson H, Ekedahl LG, Dannetun H. The effect of CO and O_2 on hydrogen permeation through a palladium membrane. Applied Surface Science 2000;153:259–67.
[100] McCool BA, Lin YS. Nanostructured thin palladium-silver membranes: effects of grain size on gas permeation properties. Journal of Materials Science 2001;36:3221–7.
[101] Uemiya S. State-of-art-the-art of supported metal membranes for gas separation. Separation and Purification Technology 1999;28:51–85.
[102] Peighambardoust SJ, Rowshanzamir S, Amjadi M. Review of the proton exchange membranes for fuel cell applications. International Journal of Hydrogen Energy 2010;35:9349–84.
[103] Pan C, He R, Li Q, Jensen J, Bjerrum N, Hjulmand H. Integration of high temperature PEM fuel cells with a methanol reformer. Journal of Power Sources 2005;145:392–8.
[104] Iulianelli A, Basile A. Sulfonated PEEK-based polymers in PEMFC and DMFC applications: a review. International Journal of Hydrogen Energy 2012;37 (15241-1525).
[105] Israni S, Harold MP. Methanol steam reforming in single-fiber bed Pd–Ag membrane reactor: experiments and modeling. Journal of Membrane Science 2011;369:375–87.
[106] Rei MH, Yeh GT, Tsai YH, Kao YL, Shiau LD. Catalysis-spillover-membrane. III: The effect of hydrogen spillover on the palladium membrane reactor in the steam reforming reactions. Journal of Membrane Science 2011;369:299–307.
[107] Sà S, Sousa JM, Mendes A. Steam reforming of methanol over a CuO/ZnO/Al_2O_3 catalyst Part II: A carbon membrane reactor. Chemical Engineering Science 2011;66:5523–30.
[108] Lee DW, Nam SE, Sea B, Ihm SK, Lee KH. Preparation of Pt-loaded hydrogen selective membranes for methanol reforming. Catalysis Today 2006;118: 198–204.
[109] Lin YM, Rei MH. Study on hydrogen production from methanol steam reforming in supported palladium membrane reactor. Catalysis Today 2001;67:77–84.
[110] Basile A, Tosti S, Capannelli G, Vitulli G, Iulianelli A, Gallucci F, et al. Co-current and counter-current modes for methanol steam reforming membrane reactor: experimental study. Catalysis Today 2006;118:237–45.
[111] Lee DW, Park SJ, Yu CY, Ihm SK, Lee KH. Study on methanol reforming-inorganic membrane reactors combined with water-gas shift reaction and relationship between membrane performance and methanol conversion. Journal of Membrane Science 2008;316:63–72.
[112] Briceño K, Iulianelli A, Montanè D, Garcia-Valls R, Basile A. Carbon molecular sieve membranes supported on non-modified ceramic tubes for hydrogen separation in membrane reactors. International Journal of Hydrogen Energy 2012;37:13536–44.
[113] Zhang X, Hu H, Zhu Y, Zhu S. Methanol steam reforming to hydrogen in a carbon membrane reactor system. Industrial & Engineering Chemistry Research 2006;45:7997–8001.
[114] Iulianelli A, Longo T, Basile A. Methanol steam reforming in a dense Pd–Ag membrane reactor: the pressure and WHSV effects on CO-free H_2 production. Journal of Membrane Science 2008;323:235–40.
[115] Itoh N, Kaneko Y, Igarashi A. Efficient hydrogen production via methanol steam reforming by preventing back-permeation of hydrogen in a palladium membrane reactor. Industrial & Engineering Chemistry Research 2002;41:4702–6.
[116] Briceño K, Montanè D, Garcia-Valls R, Iulianelli A, Basile A. Fabrication variables affecting the structure and properties of supported carbon molecular sieve membranes for hydrogen separation. Journal of Membrane Science 2012;415-416:288–97.
[117] Lin YM, Lee GL, Rei MH. An integrated purification and production of hydrogen with a palladium membrane-catalytic reactor. Catalysis Today 1998;44:343–9.
[118] Han J, Kim IS, Choi KS. High purity hydrogen generator for on-site hydrogen production. International Journal of Hydrogen Energy 2002;27:1043–7.
[119] Han J, Lee SM, Chang H. Metal membrane-type 25-kW methanol fuel processor for fuel cell hybrid vehicle. Journal of Power Sources 2002;112:484–90.
[120] Iulianelli A, Longo T, Basile A. Methanol steam reforming reaction in a Pd–Ag membrane reactor for CO-free hydrogen production. International Journal of Hydrogen Energy 2008;33:5583–8.
[121] Ghasemzadeh K, Liguori S, Morrone P, Iulianelli A, Piemonte, V. Babaluo, A.A. Basile A. H_2production by low pressure methanol steam reforming in a dense Pd-Ag membrane reactor in co-current flow configuration: experimental and modeling analysis,accepted, International Journal of Hydrogen Energy, http://dx.doi.org/10.1016/j.ijhydene.2013.06.001, in press.
[122] Ghasemzadeh, K, Liguori, S, Iulianelli, A, Morrone, P, Babaluo, AA, Basile, A. H_2 production in silica membrane reactor via methanol steam reforming: modeling and HAZOP analysis, submitted to International Journal of Hydrogen Energy, http://dx.doi.org/10.1016/j.ijhydene.2013.06.008.
[123] Basile A, Tereschenko GF, Orekhova NV, Ermilova MM, Gallucci F, Iulianelli A. An experimental investigation on methanol steam reforming with oxygen addition in a flat Pd/Ag membrane reactor,. International Journal of Hydrogen Energy 2006;31:1615–22.
[124] Chiu K-l, Kwong F-l, Ng DHL. Oxidation states of Cu in the $CuO/CeO_2/Al_2O_3$ catalyst in the methanol steam reforming process. Current Applied Physics 2012;12:1195–8.
[125] Du X, Shen Y, Yang L, Shi Y, Yang Y. Experiments on hydrogen production from methanol steam reforming in the micro-channel reactor. International Journal of Hydrogen Energy 2012;37:12271–80.
[126] Chang C-C, Wanga J-W, Chang C-T, Liaw B-J, Chen Y-Z. Effect of ZrO_2 on steam reforming of methanol over $CuO/ZnO/ZrO_2/Al_2O_3$ catalysts. Chemical Engineering Journal 2012;192:350–6.
[127] Durka T, Stefanidis GD, Van Gerven T, Stankiewicz AI. Microwave-activated methanol steam reforming for hydrogen production. International Journal of Hydrogen Energy 2011;36:12843–52.
[128] Zhang Q, Farrauto RJ. A PdZn catalyst supported on stabilized ceria for stoichiometric methanol steam reforming and hydrogen production. Applied Catalysis A: General 2011;395:64–70.
[129] Sanches SG, Flores JH, de Avillez RR, Pais da Silva MI. Influence of preparation methods and Zr and Y promoters on Cu/ZnO catalysts used for methanol steam reforming. International Journal of Hydrogen Energy 2012;37:6572–9.
[130] Jones SD, Hagelin-Weaver HE. Steam reforming of methanol over CeO_2- and ZrO_2-promoted Cu-ZnO catalysts supported on nanoparticle Al_2O_3. Applied Catalysis B: Environmental 2009;90:195–204.
[131] Yang M, Li S, Chen G. High-temperature steam reforming of methanol over $ZnO–Al_2O_3$ catalysts. Applied Catalysis B: Environmental 2011;101:409–16.
[132] Qi C, Amphlett JC, Peppley BA. Stability of NiAl layered double hydroxides derived catalysts for the steam reforming of methanol. Catalysis Communications 2009;11:71–6.
[133] Sà S, Silva H, Sousa JM, Mendes A. Hydrogen production by methanol steam reforming in a membrane reactor: palladium vs carbon molecular sieve membranes. Journal of Membrane Science 2009;339:160–70.
[134] Ouzounidou M, Ipsakis D, Voutetakis S, Papadopoulou S, Seferlis P. A combined methanol autothermal steam reforming and PEM fuel cell pilot plant unit: experimental and simulation studies. Energy 2009;34:1733–43.
[135] Patel S, Pant KK. Experimental study and mechanistic kinetic modeling for selective production of hydrogen via catalytic steam reforming of methanol. Chemical Engineering Science 2007;62:5425–35.
[136] Purnama H, Ressler T, Jentoft RE, Soerijanto H, Schlögl R, Schomäcker R. CO formation/selectivity for steam reforming of methanol with a commercial $CuO/ZnO/Al_2O_3$ catalyst. Applied Catalysis A: General 2004;259:83–94.
[137] Ritzkopf I, Vukojevic S, Weidenthaler C, Grunwaldt J-D, Ferdi Schüth. Decreased CO production in methanol steam reforming over Cu/ZrO_2 catalysts prepared by the microemulsion technique. Applied Catalysis A: General 2006;302:215–23.
[138] Olah GA, Goeppert A, Prakash GKS. Beyond oil and gas: the methanol economy. Weinheim (Germany): Wiley-VCH; 2006.
[139] [access date February 2013], ⟨http://www.ultracellpower.com/sp.php?rmfc⟩.
[140] Huck, T, Engelhardt, P, Lucka, K. Highly integrated micro fuel cell system based on a methanol steam reformer and a HT PEM fuel cell. 15th European Fuel Cell Forum. Lucern, Switzerland; 2011.
[141] Andreasen S, Kær S, Sahlin S. Control and experimental characterization of a methanol reformer for a 350 W high temperature polymer electrolyte membrane fuel cell system international. International Journal of Hydrogen Energy 2013;38:1676–84.
[142] Qi A, Peppley B, Karan K. Integrated fuel processors for fuel cell application: a review. Fuel Processing Technology 2007;88:3–22.
[143] Wichmann D, Engelhardt P, Wruck R, Lucka K, Köhne H. Development of a highly integrated micro fuel processor based on methanol steam reforming for a HT-PEM fuel cell with an electric power output of 30 W. ECS Transactions 2010;26:505–15.

[144] Boaventura M, Mendes A. Activation procedures characterization of MEA based on phosphoric acid doped PBI membranes. International Journal of Hydrogen Energy 2010;35:11649–60.
[145] Juhl AS, Knudsen KS. Modelling and evaluation of heating strategies for high temperature polymer electrolyte membrane fuel cell stacks. International Journal of Hydrogen Energy 2008;33:4655–64.
[146] Kurz T, Keller J. Heat management in a portable high temperature PEM fuel cell module with open cathode. Fuel Cells 2011;11:518–25.
[147] [access date February 2013] ⟨http://en.wikipedia.org/wiki/Honda_FCX_Clarity⟩.
[148] International Organization for Standardization, ISO/TS 14687-2, Hydrogen Fuel-Product Specification—Part 2: Proton exchange membrane Fuel Cell applications for road vehicles; 2012.
[149] Yan X, Wang S, Li X, Hou M, Yuan Z, Li D, et al. A 75-kW methanol reforming fuel cell system. Journal of Power Sources 2006;162:1265–9.
[150] Katiyar N, Kumar S, Kumar S. Comparative thermodynamic analysis of adsorption, membrane and adsorption-membrane hybrid reactor systems for methanol steam reforming. International Journal of Hydrogen Energy 2012:1–13.
[151] Basile, A, Gugliuzza, A, Iulianelli, A, Morrone, P. Membrane technology for carbon dioxide (CO_2) capture in power plants. In: Advanced membrane science and technology for sustainable energy and environmental applications, editor, A Basile and SP Nunes, Woodhead publishing Series in Energy—Cornwall (UK), 2011, Ch. 5, pp.113-159. ISBN: 978-1-84569-969-7, ISSN: 2044-9364.
[152] Iulianelli, A, Basile, A, Li, H, Van Den Brink, RW. Inorganic membranes for pre-combustion carbon dioxide (CO_2) capture. In: Advanced membrane science and technology for sustainable energy and environmental applications, editor, A Basile and SP Nunes, Woodhead Publishing Series in Energy—Cornwall (UK), 2011, Ch. 7, pp 184-213. ISBN: 978-1-84569-969-7, ISSN: 2044-9364.
[153] Harale A, Hwanga H, Liub P, Sahimi M, Tsotsis T. Experimental studies of a hybrid adsorbent-membrane reactor (HAMR) system for hydrogen production. Chemical Engineering Science 2007;62:4126–37.
[154] Ding Y, Alpay E. Equilibria and kinetics of CO_2 adsorption on hydrotalcite adsorbent. Chemical Engineering Science 2000;55:3461–74.
[155] Lee K, Beaver M, Caram H, Sircar S. Production of fuel-cell grade hydrogen by thermal swing sorption enhanced reaction concept. International Journal of Hydrogen Energy 2008;33:781–90.
[156] Hsueh C, Chu H, Yan W, Chen C. Numerical study of heat and mass transfer in a plate methanol steam micro reformer with methanol catalytic combustor. International Journal of Hydrogen Energy 2010;35:6227–38.
[157] Park G, Yim S, Yoon Y, Kim C, Seo D, Koichi E. Hydrogen production with integrated micro channel fuel processor using methanol for portable fuel cell systems. Catalysis Today 2005;110:108–13.
[158] Hsueh C, Chu H, Yan W, Leu G, Tsai J. Three dimensional analysis of a plate methanol steam micro reformer and a methanol catalytic combustor with different flow channel designs. International Journal of Hydrogen Energy 2011;36:13575–86.
[159] Telotte J, Kern J, Palanki S. Miniaturized methanol reformer for fuel cell powered mobile applications. International Journal of Chemical Reactor Engineering 2008;6:A64.
[160] Hsueh C, Chua H, Yan W, Chen C. Transport phenomena and performance of a plate methanol steam micro-reformer with serpentine flow field design. Applied Energy 2010;87:3137–47.
[161] Besser R. Thermal integration of a cylindrically symmetric methanol fuel processor for portable fuel cell power international. International Journal of Hydrogen Energy 2011;36:276–83.
[162] Bentley, JM, Mitchell, W, Clawson, L, Cross, J. US6783742B2; Aug. 31, 2004.
[163] Irving, P, Ming, Q, Harrison, J. DOE Hydrogen Program, 32 (FY2004 progress report).
[164] Sá S, Sousa J, Mendes A. Steam reforming of methanol over $CuO/ZnO/Al_2O_3$ catalyst. Part 1: Kinetic, modeling. Chemical Engineering Science 2011;20: 4913–21.
[165] Avgouropoulos G, Ioannides T, Kallitsis J, Neophytides S. Development of an internal reforming alcohol fuel cell: concept, challenges and opportunities. Chemical Engineering Journal 2011;176:95–101.
[166] Avgouropoulos G, Neophytides S. Performance of internal reforming methanol fuel cell under various methanol/water concentrations. Journal of Applied Electrochemistry 2012;42:719–26.